FINAL TECHNICAL REPORT

# "Plastic" Optoelectronics: Injection Lasers Fabricated from Soluble Semiconducting Polymers

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**14. ABSTRACT**

Report includes Principal accomplishments: Polymer Lasers, FETs with two different metals as source and drain electrodes, and Polymer FETs with high current density. A list and 1 copy of 11 publications are included. A copy of the patent filed and issued on work that resulted from support from AF49620-02-1-0127 is also included.

**15. SUBJECT TERMS**

Semiconducting Polymer FETs, LEFETs, Light Emitting FET

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*Abstract:*

Technical accomplishments include progress toward polymer lasers, successful fabrication of field effect transistors (FETs) with two different metals as source and drain electrodes, and experimental results on optically pumped Amplified Stimulated Emission (ASE) threshold of polymer films incorporated in Semiconductor-Insulator-Metal structures.

Semiconducting polymers can be characterized as laser materials by photopumping a thin-film waveguide, which can be made by casting a film on a low-refractive-index substrate. When the pump intensity is high enough for the polymer to have net gain, the spontaneously emitted photons are exponentially amplified by stimulated emission as they travel through the waveguide. Since the gain is maximal near the peak of the spontaneous emission spectrum, the spectrum exhibits '*gain narrowing*'. Consequently, an intense, spectrally narrow beam is emitted from the ends of the waveguide. Structures that exhibit ASE are sometimes referred to as 'mirrorless lasers'.

The Light Emitting FET (LEFET) is a promising route to the polymer injection laser. The FET device configuration enables improvement in the carrier injection into the semiconducting polymer and the reduction of both the absorptive losses due to the injected carriers and the absorptive losses due to the metallic electrodes. We have successfully developed the process steps required for deposition of two different metals as the source and drain electrodes, as required for the fabrication of LEFETs..

We have successfully measured the optically pumped ASE threshold of polymer films incorporated in SIM structures; i.e. in FET structures but without the source and drain electrodes. Note, however, that because the source and drain electrodes are spatially removed from the recombination zone at the center of the channel, losses from the source and drain will not be a problem. In this configuration, we have demonstrated the following:

1.  Losses from an ITO gate electrode are minimal; relatively low threshold ASE has been demonstrated in the SIM structure with M = ITO as the gate electrode material.

2.  We have discovered a new mode that propagates at the interface between the polymer and the gate dielectric in this asymmetric waveguide structure --- the "cut-off" (i.e. in addition to the usual guided mode). The cutoff mode exhibits gain at relatively low pump powers

If the cutoff mode propagates exactly in the recombination zone for electrons and holes in the LEFET structuree, the optical confinement parameter should be close to unity. Based upon these results and analyses, we expect that in an electrically pumped LEFET, amplified spontaneous emission and lasing will be more easily achieved at the wavelength of the cut-off mode.

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**Principal Accomplishments**

*Polymer Lasers*

Polymer light emitting materials are attractive gain media for use in semiconducting lasers. Semiconducting polymers can be characterized as laser materials by photopumping a thin-film waveguide, which can be made by casting a film on a low-refractive-index substrate. When the pump intensity is high enough for the polymer to have net gain, the spontaneously emitted photons are exponentially amplified by stimulated emission as they travel through the waveguide. Since the gain is maximal near the peak of the spontaneous emission spectrum, the spectrum exhibits *'gain narrowing'* [F. Hide *et al*, Science 237, 1833 (1996)]. Consequently, an intense, spectrally narrow beam is emitted from the ends of the waveguide. Structures that exhibit ASE are sometimes referred to as 'mirrorless lasers'. Most of the characterization of semiconducting polymers for laser development has been done with mirrorless laser structures with a clear understanding that the polymer gain medium can be incorporated into a resonant structure once the materials have been optimized.

Optically pumped conjugated polymer lasers are characterized by a threshold for lasing as small as $100W/cm^2$. Assuming 10% internal quantum efficiency for the electroluminescence, we have estimated that the current density required to achieve a comparable excitation density to the one obtained with photo pumping intensity of $100W/cm^2$ is about $100A/cm^2$. Current densities of this magnitude are attainable: Current densities two orders of magnitude greater than $100A/cm^2$ have been demonstrated in FETs fabricated from semiconducting polymers [G. Wang *et al*, J. Appl. Phys. 95, 316 (2004)]. Moreover, when driving typical Polymer LEDs with pulsed bias, the transient current can be increased by many orders of magnitude above the damage threshold of dc current [D. Braun *et al*, Appl. Phys. Lett. 61, 3092 (1992)].

The Light Emitting FET (LEFET) is a promising route to the polymer injection laser. The FET device configuration enables improvement in the carrier injection into the semiconducting polymer and the reduction of both the absorptive losses due to the injected carriers and the absorptive losses due to the metallic electrodes. The gate-induced carrier injection into the FET channel leads to a high density of carriers near the source and drain electrodes. Carrier accumulation at the polymer-metallic electrode interfaces narrows the potential barrier widths and thereby facilitates the carrier injection.

For operation of an FET as a LEFET, there are two criteria:

1. The semiconducting, luminescent polymer in the channel of the FET must be capable of operation both n-channel operation (electron injection and transport) and p-channel operation (hole injection and transport).

2. The LEFET device operation requires balanced injection --- electrons at the source and holes at the drain (or vice versa). This requires the use of two different metals with Fermi energies that match the $\pi$-band and $\pi^*$-band of the polymer, respectively. Thus, the source must be fabricated from a low work function metal such as Ba or Yb (to enable electron injection) while the drain must be fabricated from a high work function metal such as Au (to enable hole injection).

3. To exceed the ASE threshold in the LEFET will require relatively high current
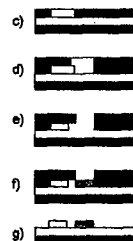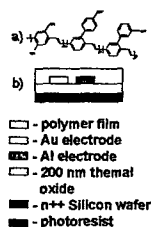
density.


## FETs with two different metals as source and drain electrodes:

As shown in the following diagram, we have developed the process steps required for deposition of two different metals as the source and drain electrodes.

Need Capability to Fabricate source and drain from different metals

Fabrication processes
Worked out in our labs
and ready to go!



- polymer film
- Au electrode
- Al electrode
- 200 nm themal
  oxide
- n++ Silicon wafer
- photoresist

Procedure for fabricating source and drain electrodes form different metals
in the top-contact configuration has also been developed. Top-contact
configuration may be better for LEFET.


## Polymer FETs with high current density

High current density devices have been demonstrated using high dielectric constant insulators as the gate dielectric. Since the FET is in essence a capacitor in which the induced charges within the semiconductor (near the semiconductor-insulator interface) are mobile, the current density in the channel is proportional to the density of carriers [G. M. Wang $et\ al$, J Appl. Phys. 93, 6137 (2003)]. In the linear regime, the density of gate-induced carriers per unit area of the channel, $N_c$, is given by

$$N_c = (\varepsilon/ed)\, V_G$$

where e is the electron charge, d is the thickness of the gate dielectric, and $V_G$ is the gate voltage. Thus, one expects higher current densities when high dielectric constant materials such as $TiO_2$ ($\varepsilon = 41$) as the gate insulator. As shown in the following Figure, we have succeeded in demonstrating high performance polymer FETs with $TiO_2$ as the gate insulator [G. M. Wang $et\ al$, J. Appl. Phys. 95, 316 (2004)].

# FET using TiO$_2$ ($k$=41) layer as the gate insulator

- TiO$_2$ ($k$=41) layer as the gate insulator.
- RR-P3HT as the electronically active semiconductor

[Heeger group, J. Appl. Phys. 93 (2003)]
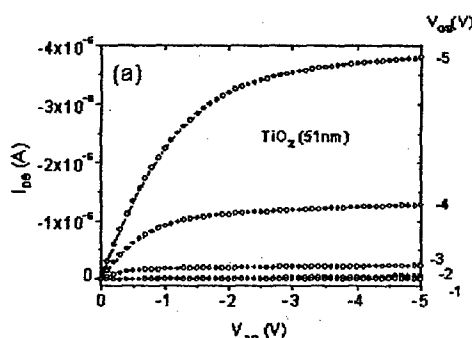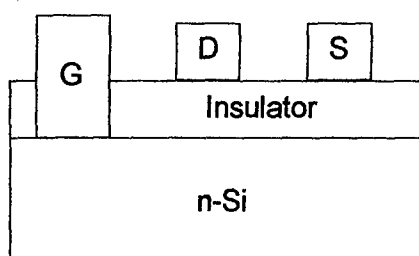


L=5 μm, W = 1000 μm, μ = 0.01 cm$^2$/V-s

Note that for $V_G$ = 5V, the source drain current is 4 μA at a $V_{SD}$ = 5V ($V_{SD}$ = source drain votage) with channel width of 0.01 cm and channel length of 5 μm. Since the current in the channel is confined to a few monolayers (approx 20 x 10$^{-8}$ cm) the current density is 2x10$^{+3}$ A/cm$^2$ --- sufficiently high to exceed that estimated for achieving ASE!.

*Thus, our expertise in semiconducting polymer FETs will be utilized for the design, fabrication, and characterization of the LEFETs.*

Finally, in recent work we have measured the optically pumped ASE threshold of polymer films incorporated in SIM structures; i.e. in FET structures but without the source and drain electrodes [M. Pauchard *et al*, Appl. Phys. Lett. 83, (2003)]. Note, however, that because the source and drain electrodes are spatially removed from the recombination zone at the center of the channel, losses from the source and drain will not be a problem. In this configuration, we have demonstrated the following:

1. Losses from an ITO gate electrode are minimal; relatively low threshold ASE has been demonstrated in the SIM structure with M = ITO as the gate electrode material.

2. We have discovered a new mode that propagates at the interface between the polymer and the gate dielectric in this asymmetric waveguide structure --- the "cut-off" (i.e. in addition to the usual guided mode). The cutoff mode exhibits gain at relatively low pump powers as shown in the following Figures:
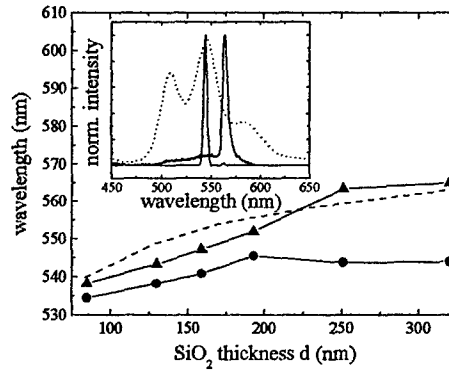
ASE wavelength of the guided mode (circles) and the wavelength of the cut-off mode (triangles), observed below threshold power of the guided mode, vs. SiO$_2$ thickness. Calculated cut-off wavelength of the system (dashed line) [9]. *Inset:* Edge emission spectra of a SIM structure with 250 nm thick SiO$_2$ gate insulator at high (left) and low (right) pump powers and emission spectrum of BOP-PPV as reference (dotted line) [M. Pauchard *et al*, Appl. Phys. Lett. 83, (2003)].

## Gain observed for the cut-off mode in S-I-M structure
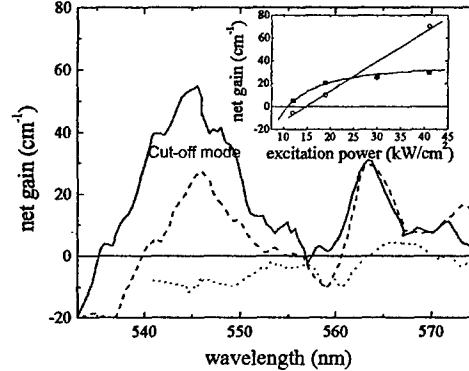


Gain spectra obtained from a SIM structure with 250 nm thick gate insulator, measured at a pump power of 12 kW/cm$^2$ (dotted), 30 kW/cm$^2$ (dash-dotted) and 41 kW/cm$^2$ (solid).
*Inset:* Net gain at the wavelength 545 nm (open circles) and 563 nm (squares).
The solid lines are a guide to the eye.

The net gain g($\lambda$) of the emitted light in this waveguiding structure is given by

$$g(\lambda) = \Gamma(\lambda) \cdot g_{mat}(\lambda) - \alpha_i(\lambda) \tag{1}$$

with g$_{mat}$($\lambda$) being the material gain, $\Gamma(\lambda)$ the optical confinement factor, and $\alpha_i(\lambda)$ the scattering losses of the waveguide, respectively. g$_{mat}$($\lambda$) is related to the density of states, DOS($\lambda$), as qualitatively represented by the emission spectrum of the polymer, and the re-absorption losses introduced by the spectral overlap of the absorption and emission

spectrum. Note that $\Gamma(\lambda)$ describes how well the material gain is coupled to the emission region.

For luminescent semiconducting polymers, $g_{mat}(\lambda)$ is highest at the emission maximum (for BOP-PPV at 545 nm). The scattering losses $\alpha_i(\lambda)$ can be considered independent of the wavelength and the re-absorption does not play an important role in the spectral region around 545 nm. The dominating wavelength is therefore determined by the maximum of the product $\Gamma(\lambda) \times DOS(\lambda)$.

A good description of the detected ASE intensity $I(\lambda,L)$ after propagating a length L at an emission wavelength $\lambda$ can be derived by describing the system as an ideal one dimensional amplifier. A certain fraction of the spontaneous emission $I_{sp}$, which is determined through the spontaneous emission factor $\beta$, is coupled into the guided amplifier mode. These photons can induce stimulated emission along a single pass L through the excited waveguide. The change of the intensity along z is given by

$$\frac{I(\lambda,z)}{dz} = \beta\, I_{sp}(\lambda) + g(\lambda)I(\lambda,z) \qquad (2)$$

If saturation effects can be neglected up to the stripe length L, the solution to Eq. (2) is

$$I(\lambda,L) = \frac{\beta\, I_{sp}(\lambda)}{g(\lambda)}\left(e^{g(\lambda)L} - 1\right) \qquad (3)$$

which corresponds to a nearly exponential increase of the ASE intensity with increasing stripe length L (in case of positive optical gain $g(\lambda)$).

If the cutoff mode propagates exactly in the recombination zone for electrons and holes in the LEFET structuree, the optical confinement parameter should be close to unity. Based upon these results and analyses, we expect that in an electrically pumped LEFET, amplified spontaneous emission and lasing will be more easily achieved at the wavelength of the cut-off mode. Μορεοτσερ, βεχαυσε τηε χυτ–οφφ μοδε τραχκσ $\lambda_{cut-off}$, controlling the thickness of the gate insulator or the polymer film provides tuneability of the wavelength, without any increase of the laser threshold [M. Pauchard et al, Appl. Phys. Lett. 83, (2003)].

# The following publications listed support from this AFOSR Grant (AF49620-02-1-0127)

Light amplification in polymer field effect transistor structures, M. Pauchard, J. Swensen, D. Moses, A.J. Heeger, J. of Applied Physics 94 (N5) 3543-3548 (2003).

Origin of efficient light emission from a phosphorescent polymer/organometallic guest-host system, R.A. Negres, X. Gong, J.C. Ostrowski, G.C. Bazan, D. Moses, A.J. Heeger, Physical Review B 68 (N11) 115209 (2003).

Time-resolved measurements of photoinduced electron transfer from polyfluorene to C60, Q.-H. Xu, D. Moses, A.J. Heeger, Physical Review B 67 (24) 245417 (2003).

Direct observation of a time-delayed intermediate state generated via exciton-exciton annihilation in polyfluorene, Q.-H. Xu, D. Moses, A.J. Heeger, Physical Review B 68 (N17) 174303 (2003).

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Red electrophosphorescence from polymer doped with iridium complex, X. Gong, J.C. Ostrowski, G.C. Bazan, D. Moses, A.J. Heeger, Applied Physics Letters 81 (N20) 3711-3713 (2002).

High-Efficiency Polymer-Based Electrophosphorescent Devices, X. Gong, M.R. Robinson, J.O. Ostrowski, D. Moses, G.C. Bazan, A.J. Heeger, Adv. Mater. 14 (N8) 581-585 (2002).

Delayed emission from recombination of charge separated pairs on polyfluorene chains in dilute solution, Q.-H. Xu, D. Moses, A.J. Heeger, Physical Review B, 69 (11) 113314 (2004).

**The following patent was filed and issued on work that resulted from support from AF49620-02-1-0127**

U.S. Patent 6,828,583 B2
Date of Issue: December 7, 2004
Title: "Injection Lasers Fabricated from Semiconducting Polymers"
Inventors: Alan J. Heeger, Marc Pauchard-Strebel, Martin Vehse, Ludvig Edmann and Daniel Moses

Copies of all of the publications listed above and a copy of the issued patent listed above are included as part of this Final Technical Report

# Delayed emission from recombination of charge-separated pairs on polyfluorene chains in dilute solution

Qing-Hua Xu, Daniel Moses, and Alan J. Heeger

*Institute for Polymers and Organic Solids, University of California, Santa Barbara, Santa Barbara, California 93106, USA*

We report the observation of delayed emission (approximately 400 ps with respect to the excitation pulse) from polyfluorene in dilute solution at high excitation intensities. Photoinduced absorption (with initial amplitude superlinearly dependent on the excitation intensity) is also observed with almost instantaneous onset and subpicosecond initial decay, followed by a slow component that decays on the time scale of 200–400 ps. The results are interpreted in terms of generation of charge-separated pairs via dissociation of a higher-energy excited state (created by sequential absorption within the pump pulse) and subsequent recombination of the charged-separated pairs into neutral excitons, which are responsible for the delayed emission. The insensitivity of these features to the concentration and to the use of different solvents confirms their intrachain origin.

Semiconducting polymers have emerged as materials with interesting optical and electronic properties and promising applications, including light-emitting diodes, lasers, field effect transistors, and solar cells.[1,2] Extensive research has been carried out with the goal of understanding the photophysics of this class of materials, and a number of different mechanisms have been proposed for the photogeneration of charged, mobile carriers.[3] Studies of poly(phenylene vinylene) (PPV) and its soluble derivatives showed that both neutral excitons and charge-separated pairs (polaron pairs) are generated within 100 fs following direct $\pi$-$\pi^*$ photoexcitation.[4,5] Charge-separated pairs can also be generated in polymer films via the dissociation of a higher-energy excited state, prepared either by sequential absorption within the pump pulse[6–12] or by exciton-exciton annihilation.[13,14]

Recent studies of semiconducting polymers have focused on polyfluorene and its soluble derivatives—for example, poly(9,9-dioctylfluorene) (PFO), a blue-emitting polymer with high-efficiency photoluminescence.[15] Although studies of the dynamical properties of polyfluorene films have been frequently revisited,[6–9,11,13,14] little attention has been paid to the ultrafast photophysics of PFO in solution.

Here we present the observation of delayed emission (approximately 400 ps with respect to the excitation pulse) from macromolecular PFO chains in dilute solutions at high excitation intensities by ultrafast pump-probe measurements. At high excitation intensities, photoinduced absorption with initial amplitude superlinearly dependent on the excitation intensity is also observed with almost instantaneous onset and subpicosecond initial decay, followed by a slow component that decays on the time scale of 200–400 ps. This nonlinear photoinduced absorption is observed within the wavelength range where transient absorption associated with a higher-energy excited state and charge-separated pairs were previously reported.[6–9,11,13,14] These observations suggest that the delayed emission likely arises from the recombination of charge-separated pairs that are generated via the dissociation of a higher-energy excited state created by sequential two-photon absorption of the pump pulse.

The instrumentation for ultrafast pump-probe measurements has been described in detail elsewhere.[16] The 400-nm pump beam is focused onto the sample with a beam size of 300 $\mu$m and overlaps the smaller-diameter ($\sim$100-$\mu$m) probe beam (continuum white light). In order to minimize interchain interactions, the concentration of the polyfluorene/toluene solution was kept low (o.d.$\sim$3 for 1 mm path length at the wavelength of maximum absorption, $\sim$3 $\times 10^{-4}$ wt/wt).

Ultrafast pump-probe experiments measure the transmission change of the probe pulse modulated by the pump pulse—i.e., $\delta T/T$. The $\delta T/T$ signal is positive for stimulated emission (SE) and negative for photoinduced absorption (PA). The photoinduced transient spectrum can be reconstructed from single-wavelength measurements. The transient spectra observed from PFO in dilute solution [Fig. 1(a)] are similar to those obtained from thin films of the same material.[9,16–18] The pump-probe signal is dominated by stimulated emission (i.e., the signal is positive) for probe wavelengths on the red side of the absorption spectrum (400–490 nm), but the SE is overwhelmed by photoinduced absorption beyond 490 nm (i.e., the signal becomes negative). However, the dynamical behavior of the photophysics for PFO chains in dilute solution displays a different pump intensity dependence from that in films.

In films, the initial decay of the SE signal becomes faster as the pump intensity increases as a result of exciton-exciton annihilation.[6,9,11,13,17] In contrast, only a subtle change is observed in the initial decay of the SE signal probed at 450 nm in the PFO/toluene solution as the pump intensity increases [Fig. 1(b); data are normalized at maximum intensities]. Instead, an additional feature appears at longer delay times (on the time scale of several hundred picoseconds) at high excitation intensities, indicating delayed emission from neutral excitons. Fitting of the data obtained at low excitation intensities gives an average exciton lifetime of $\sim$250 ps. However, at 0.36 $\mu$J, significant delayed emission is observed at 400–500 ps. At even higher excitation intensities (0.50 $\mu$J), the delayed emission becomes less pronounced.

In our opinion, the concept of fully vapor-deposited thin-layer TiO$_2$ solar cells presented here opens a very promising approach in the expanding field of solar cell research, to achieve inexpensive and stable devices for large field of application. This cell fabrication method enables a direct integration in the existing technology of vapor-deposited electro-optic thin-layer devices. We believe that the performance of TiO$_2$ cells under solar conditions can be further improved by the use of narrow bandgap dyes, with the aims of expanding the spectral absorption domain and to match the photon flux spectrum of the Sun. Furthermore, by suitable device engineering the interface area between TiO$_2$ and the dye responsible for charge separation can be increased, resulting in more efficient devices. Moreover, the limitation caused by the very small diffusion length of charge carriers, in the range of 10 nm, can be overcome by optimizing the individual layer thicknesses in the device into the same range as the diffusion length of charge carriers. The concepts of increased light harvesting as recently demonstrated in vapor-deposited thin-layer cells by Forrest et al.[3] and the use of dopants[2] to decrease the series resistance in the device can also lead to improved device performance.

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# High-Efficiency Polymer-Based Electrophosphorescent Devices**

By *Xiong Gong, Matthew R. Robinson, Jacek C. Ostrowski, Daniel Moses, Guillermo C. Bazan,* and *Alan J. Heeger*

Organic light-emitting diodes (OLEDs) are under active investigation because of their potential for application in flat panel displays.[1,2] Research on OLEDs has focused on the improvement of the emission efficiency by developing high-efficiency fluorescent materials and on the use of novel device architectures.

The existence of an upper limit for the electroluminescence (EL) internal quantum efficiency (QE) has been widely discussed. Since charge carrier recombination in π-conjugated systems can produce both emissive singlet and non-emissive triplet excited states, a simple statistical argument leads to an upper limit for the internal QE of 25 %.[3] The 25 % upper limit assumes similar cross sections for the formation of singlets and triplets.[4] Experiments have recently shown, however, that in luminescent semiconducting polymers, the singlet cross section is considerably larger than the triplet cross section (by a factor of 3–4).[5] As a result, electroluminescent quantum efficiencies as high as 50 % have been reported.[3] Nevertheless, by utilizing a phosphorescent dye that captures both singlet and triplet excited states, the OLED internal efficiency can, in principle, be increased to 100 %.

Utilization of the triplet excitations in OLEDs was proposed several years ago.[6,7] These devices incorporate a heavy metal atom with strong spin–orbit coupling that enhances intersystem crossing and mixes the singlet and triplet states. In this way, the lowest triplet state is efficiently populated and can produce light emission via phosphorescence. Recently, electrophosphorescent OLEDs based on small molecules as the transport materials have achieved considerable success.[8,9,10,11] For example, an external quantum efficiency (QE$_{ext}$) of 13.7 % and power efficiency of 38.3 lm/W at 0.215 mA cm$^{-2}$ were reported using [Ir(ppy)$_3$] as the phosphorescent dopant for green-light

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# Ultrafast charge photogeneration in conjugated polymers

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## Abstract

The mechanism for ultrafast charge generation in poly(paraphenylene-vinylene) – PPV and its soluble derivatives has been investigated by pump-probe spectroscopy. The quantum yield for charge generation ($\phi_{ch}$) as a function of pump photon energy has been measured by exciting the samples with ultrashort pulses (2.2 to 6.2 eV, ~ 100 fs pulsewidth) and probing the photoinduced absorption of infrared-active vibrational modes (IRAV). The ultrafast nature of charge generation, the significant quantum yield observed ($\phi_{ch}$ ~ 0.1) and its weak photon energy dependence suggest that polarons are primary photoexcitations of conjugated polymers.

*Keywords:* Time-resolved fast spectroscopy, Photoinduced absorption spectroscopy, Optical absorption and emission spectroscopy, Photoconductivity, Poly(phenylene vinylene) and derivatives.

## 1. Introduction

Conjugated polymers have been extensively studied for over twenty years since they are low-dimensional molecular systems exhibiting interesting electronic and optical properties with many potential applications in electronics and optoelectronics [1]. Despite all the advances, many fundamental issues continue to be highly controversial, such as the exciton binding energy and the nature of their primary photoexcitations [2].

In particular, the mechanism for charge generation in conjugated polymers is still debatable. Many researchers believe that excitons are primary photoexcitations and that polarons result from exciton dissociation [3,4] or bimolecular decay of excitons [5]. We have recently observed ultrafast charge photogeneration with significant quantum efficiency ($\phi_{ch}$ ~ 0.1), suggesting that polarons can be produced directly by photoexcitation [6]. However, it has been proposed that carriers can be generated in ultrafast time-scales by a two-step optical excitation followed by exciton dissociation [7]. In this paper we present the wavelength dependence of the quantum efficiency for ultrafast charge photogeneration. The results address the key issues related to the charge generation mechanism and exciton binding energy in conjugated polymers.

## 2. Experimental Technique

The ultrafast charge generation in conjugated polymers was probed by pump-probe spectroscopy. The samples were excited by ultrashort pulses tuneable from 2.2 to 6.2 eV and probed by mid-infrared pulses tuneable between 1000 and 3000 cm$^{-1}$. The photoinduced absorption in the mid-infrared has spectral features due to infrared-active vibrational modes (IRAV). The IRAV modes are well-known probes of charged excitations in conjugated polymers [8]; they become evident upon chemical doping [9] and they are not sensitive to neutral excitons. The intensity of the IRAV modes is therefore a unique probe for carrier generation in semiconducting polymers.

Measurements were carried out on samples of poly(paraphenylene-vinylene) – PPV and poly(2-methoxy,5-(2'-ethyl-hexyloxy) paraphenylene vinylene) – MEH-PPV. The PPV samples were freestanding films of stretch-aligned PPV ($l/l_0$ = 4, ~ 15 μm thick). The MEH-PPV samples were also freestanding films obtained either by dropcasting or multiple spin casting from aromatic solvents and subsequent detachment from the substrate (1 to 40 μm thick).

## 3. Results and Discussion

The mid-infrared spectral dependence of the photoinduced absorption was measured for pristine MEH-PPV and for a blend of MEH-PPV and C$_{60}$ (50% w/w C$_{60}$). The C$_{60}$ – MEH-PPV blend is known to undergo ultrafast electron transfer from polymer to C$_{60}$ and therefore produce polarons with nearly 100% quantum efficiency [10]. In both samples the spectral dependence obtained by the

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# Red electrophosphorescence from polymer doped with iridium complex

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We demonstrate efficient, bright red electrophosphorescent light emitting diodes (LEDs) employing tris (2,5-bis-2'-(9',9'-dihexylfluorene) pyridine) iridium (III), [Ir(HFP)$_3$], doped into a blend of poly(vinylcarbazole) (PVK) with 2-*tert*-butylphenyl-5-biphenyl-1,3,4-oxadiazol (PBD). At a current density of 2.35 mA/cm$^2$ (brightness of 169 cd/m$^2$), the external quantum efficiency ($QE_{ext}$) and luminous efficiency (*LE*) were 5% ph/el and 7.2 cd/A, respectively. Even at 50 mA/cm$^2$, $QE_{ext}$=3.4% ph/el and *LE*=5.2 cd/A. The electroluminescent emission is characteristic of Ir(HFP)$_3$, with maximum at 600 nm. The devices exhibited no emission from either PVK or PBD, even at the lowest concentration of Ir(HFP)$_3$ (0.05 wt%). The results demonstrate that electrophosphorescence with high brightness and efficiency can be achieved from polymer-based LEDs fabricated by processing the active materials from solution. © *2002 American Institute of Physics.* [DOI: 10.1063/1.1511283]

Organic light emitting diodes (OLEDs) continue to be actively investigated because of their potential for applications in flat panel displays, particularly for portable electronic devices.[1,2] Research on OLEDs has focused on the improvement of the emission efficiency by developing high efficiency fluorescent materials and the use of novel device architectures. By utilizing triplet-based emitting centers in OLEDs, and thereby capturing both singlet and triplet excited states, the internal quantum efficiency can, in principle, be increased to 100%.[3,4]

The utilization of triplet emitters to improve OLED efficiency was proposed by several groups.[5–7] Recently, considerable progress has been demonstrated with electrophosphorescent OLEDs based on small molecules as the host materials.[8–10] For example, external quantum efficiency ($QE_{ext}$) of 13.7% and power efficiency of 38.3 lm/W at 0.215 mA/cm$^2$ were reported using Ir(ppy)$_3$ as the phosphorescent dopant for green light emission.[9] Lamansky *et al.* reported $QE_{ext}$=12.3% in devices fabricated by co-evaporating an iridium complex and 4,4'-N,N'-dicarbazolebiphenyl in a multilayer structure.[11]

Electrophosphorescent OLEDs based on polymers as the host materials are important because they can be fabricated at room temperature by processing the materials from solution; for instance, by spin-casting, screen-printing, or inkjet-printing.[7,12–16] Lee *et al.*[12] reported $QE_{ext}$=1.9% ph/el and a brightness of 2500 cd/m$^2$ for Ir(ppy)$_3$-doped poly(vinylcarbazole) (PVK) devices with 3-(4-biphenyl)-4-phenyl-5-tert-butylphenyl-1,2,4-triazole as a hole-blocking layer. O'Brien *et al.*[13] reported PtOEP-doped polyfluorene devices with maximum $QE_{ext}$=3.5% ph/el. Zhu *et al.*[15] reported $QE_{ext}$=5.1% ph/el and luminous efficiency (LE) of 12 cd/A obtained by incorporating the phosphorescent dopant,

Ir(Bu-ppy)$_3$ doped into CN-PPP for green light emission. In our previous work, $QE_{ext}$ of 10% ph/el and *LE* of 36 cd/A were achieved by doping tris [9,9-dihexyl-2-(pyridnyl-2') fluorene)] iridium (III) ([Ir(DPF)$_3$]) into a blend of PVK with 2-*tert*-butylphenyl-5-biphenyl-1,3,4-oxadiazol (PBD).[16]

The quantum efficiency of electrophosphorescent LEDs based on polymers is still relatively low compared to results obtained from electrophosphorescent LEDs prepared by vapor deposition of small molecules. Moreover, achieving red electrophosphorescence from iridium complexes[11,17] represents an important step toward full color applications.

In order to achieve red emission and improve the performance of polymer based red electrophosphorescent LEDs, we synthesized the iridium complex, tris (2,5-bis-2'-(9',9'-dihexylfluorene) pyridine) iridium (III), [Ir(HFP)$_3$] [Fig. 1(a) inset].[18] By coupling two fluorene units at the *ortho* position on the pyridine ring, solid-state quenching is minimized,[18] and electron–hole trapping on the Ir complex is improved.[19] Using a blend of PVK–PBD [Fig. 1(a) inset] as
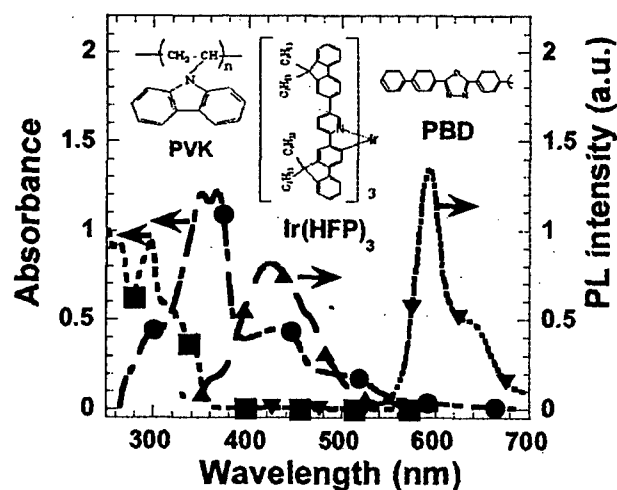


FIG. 1. Normalized spectra: Absorption spectra of thin films of PVK-PBD (40 wt%) (■) and pure Ir(HFP)$_3$ (●); photoluminescence spectra of thin films of PVK–PBD (40 wt%) (▲) and pure Ir(HFP)$_3$ (▼). Inset: the molecular structures of Ir(HFP)$_3$, PVK, and PBD.

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# Ultrafast charge photogeneration in conjugated polymers

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## Abstract

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The ultrafast charge generation in conjugated polymers was probed by pump-probe spectroscopy. The samples were excited by ultrashort pulses tuneable from 2.2 to 6.2 eV and probed by mid-infrared pulses tuneable between 1000 and 3000 cm⁻¹. The photoinduced absorption in the mid-infrared has spectral features due to infrared-active vibrational modes (IRAV). The IRAV modes are well-known probes of charged excitations in conjugated polymers [8]; they become evident upon chemical doping [9] and they are not sensitive to neutral excitons. The intensity of the IRAV modes is therefore a unique probe for carrier generation in semiconducting polymers.

Measurements were carried out on samples of poly(paraphenylene-vinylene) – PPV and poly(2-methoxy,5-(2'-ethyl-hexyloxy) paraphenylene vinylene) – MEH-PPV. The PPV samples were freestanding films of stretch-aligned PPV ($l/l_0$ = 4, ~ 15 μm thick). The MEH-PPV samples were also freestanding films obtained either by dropcasting or multiple spin casting from aromatic solvents and subsequent detachment from the substrate (1 to 40 μm thick).

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# Light amplification in polymer field effect transistor structures

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The amplified spontaneous emission (ASE) of optically pumped films of poly(2-(2',5'-bis(octyloxy)benzene)-1,4-phenylenevinylene (BOP-PPV) was studied in structures comprising a gate electrode, a thin film of gate insulator material ($SiO_2$) and the polymer film as luminescent semiconducting layer (i.e. a field effect transistor without the source and drain electrodes). The influences of different gate electrodes on the threshold and the wavelength of the amplified emission were measured for variable thickness of the gate insulator. An exponential increase in ASE threshold ($I_t$) with decreasing separation between electrode and polymer layer was observed. In structures with 200 nm $SiO_2$ gate insulator, $I_t = 300$ kW/cm$^2$ with an $n$-Si gate electrode and 200 kW/cm$^2$ with Au electrode (100 nm thick). Compared to the same polymer film on pure $SiO_2$ ($I_t = 2$ kW/cm$^2$), this increase results from waveguide losses in the nearby gate electrode. With an indium–tin–oxide (ITO) gate electrode (140 nm thick) on glass, again with a 200 nm $SiO_2$ gate insulator, $I_t = 30$ kW/cm$^2$. The ITO electrode acts as a second waveguide, and the light is distributed into two modes. The observed wavelength shift and the increasing $I_t$ with decreasing $SiO_2$ thickness result from this mode structure. When the thickness of the ITO electrode is less than 60 nm, the mode traveling mainly in the ITO is cutoff, and a single waveguide structure is formed with an associated reduction in $I_t$. For an ITO thickness of 12 nm, $I_t = 4$ kW/cm$^2$, only two times bigger than that observed in a pure BOP-PPV film on fused silica. © *2003 American Institute of Physics.* [DOI: 10.1063/1.1597957]

## INTRODUCTION

Organic light emitting materials are attractive gain media for use in semiconductor lasers. Optically pumped laser action has been demonstrated in a broad range of materials in many different configurations.[1–5] Low threshold optically pumped lasers have been fabricated from luminescent organic semiconductors with emission wavelengths ranging over the entire visible spectrum. The realization of electrically pumped injection lasers represents a greater challenge; the complex interplay of optical and electronic properties make great demands on the material properties and the device structure.[6] In analogy with organic light emitting diodes one of the most obvious approaches to the injection laser is to use a vertical cavity laser configuration in which the active material is a thin film between two electrodes. However, the presence of a metal electrode in direct contact with a laser active polymer material leads to a significant increase of the lasing threshold: 19 000 kW/cm$^2$ (MEH-PPV in a DFB structure with a Ag electrode)[7] compared to 1 kW/cm$^2$ (BuEH-PPV on $SiO_2$ in a DFB structure).[8]

Although cladding layers can be used to separate the electrode from the gain region, a cladding layer thickness of 300–500 nm would be required to sufficiently reduce the losses introduced by the Ag electrodes.[3] Because of the rather low mobility of charge carriers in organic materials, charge transport through such thick cladding layers is a huge problem. In addition, the driving voltage will increase with the overall device thickness. By using thin transparent indium–tin–oxide (ITO) contact layers, the waveguide losses were reduced significantly ($\alpha < 300$ cm$^{-1}$).[9] Very high current densities were achieved in such devices. However, because of the high density of charge carriers in the device, the charge-induced absorption (by polarons) increased with increasing pump current and lasing was not observed. Charge induced absorption will be a problem in organic materials whenever the carriers are injected through the "gain" medium and carrier-induced losses overlap the spectral region of the emission.[6]

A different and promising device configuration is the light emitting field effect transistor (FET). The FET approach avoids the above mentioned problems by separating the electrodes (source and drain) from the waveguiding gain material and by arranging the charge injection and transport perpendicular to the waveguide structure. In the FET, the only electrode that can introduce losses into the waveguide is the gate electrode which is separated from the gain region by the gate insulator (e.g., $Al_2O_3$ or $SiO_2$).

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# Optical amplification of the cutoff mode in planar asymmetric polymer waveguides

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Modes with low threshold for optical gain were observed at wavelengths close to the cutoff in experiments probing the amplified spontaneous emission of light-emitting polymer thin films. The polymer was the semiconductor layer in a multilayer semiconductor–insulator–metal structure that simulates the one-dimensional waveguide characteristics in the channel of a field-effect transistor. The "cutoff" mode propagates at the polymer/gate-insulator interface, has an optical gain threshold of approximately $10 \, kW/cm^2$, and is not influenced by absorption of the gate electrode. The wavelength of the amplified emission tracks the cutoff wavelength of the asymmetric double-waveguide structure and the cutoff mode is, therefore, tunable in wavelength. Our results suggest that the light-emitting field-effect transistor architecture is a promising route for the construction of an injection laser. © *2003 American Institute of Physics.*
[DOI: 10.1063/1.1627477]

Since the discovery of laser action in conjugated polymers in 1992,[1] remarkable progress has been made in implementing semiconducting polymers into different resonant structures for optically pumped lasers.[2,3] In analogy with organic light-emitting diodes, one of the most obvious approaches to the electrical injection laser is to use a sandwich configuration in which the active material is a thin film between two electrodes.[4,5] Despite the fact that threshold current densities estimated from the excitation density required for optically pumped lasers have been exceeded in polymer diode structures by an order of magnitude,[6,7] electrically pumped laser emission has not been demonstrated. The losses in the electrically pumped devices are higher than in simple photopumped waveguides because of two additional loss mechanisms: losses introduced by the metal electrodes and charge-carrier (polaron)-induced absorption.[2] The light-emitting field-effect transistor (LEFET) structure, proposed in 2000, offers important advantages as a route to the organic injection laser.[8] The electrode losses will be reduced by the FET structure with gate-induced injection through the source and drain. Since the transport of injected charge carriers is perpendicular to the optical confinement, the reduced density of charged polarons in the light propagation pathway leads to a reduction in the carrier-induced absorption losses. Thus, although the LEFET has not yet been demonstrated, the LEFET architecture is a promising approach for realizing the electrically pumped injection laser.[8] For this reason, the present study investigates the optical gain and threshold behavior of the optical modes appearing in special asymmetric waveguide structure and demonstrates the discovery of optical amplification with a low threshold for the cutoff mode.

The samples investigated were semiconductor–insulator–metal (SIM) multilayer structures; that is, FET structures without source and drain electrodes, as schematically shown in Fig. 1. ITO was used for the gate electrode, because a recent study has demonstrated that this material introduces only small losses compared to other electrode materials (e.g., Au or $n$-Si).[9] Therefore, 140-nm-thick ITO electrodes were sputtered onto BK7-glass substrates and subsequently covered by $SiO_2$ insulator films of different thicknesses ($d$). On top of the $SiO_2$ insulating layer, a film (150 nm thick) of the light-emitting polymer, poly(2-(2′,5′-bis(octyloxy)benzene)-1,4-phenylenevinylene) (BOP-PPV),[10] was spin-cast from a 1% p-xylene solution. The refractive indices of the ITO ($n_4 \approx 1.99$) and the polymer ($n_2 \approx 1.77$) are higher than that of air ($n_1 \approx 1.00$), the gate insulator $SiO_2$ ($n_3 \approx 1.46$), and the BK7-glass substrate ($n_5 \approx 1.52$), respectively. Therefore, this SIM structure forms an asymmetric double waveguide. The index profile of the waveguide and the mode intensities of the two guided TE modes propagating parallel to the substrate are shown on the right-hand side of Fig. 1. The optical gain and the amplified spontaneous emission (ASE) were measured using the vari-
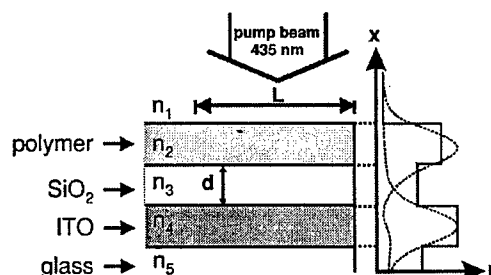


FIG. 1. Cross section of the waveguide structure. $d$ is the thickness of the gate oxide $SiO_2$ and $L$ is the length of the pump stripe used for optical excitation. On the right: Refractive index profile and mode intensities of the two supported TE modes of the waveguide.

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# Excitation spectrum for ultrafast photogeneration of charged solitons in polyacetylene

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Ultrafast photoinduced absorption by infrared-active vibrational modes is used to detect charged solitons in oriented *trans*-polyacetylene. Soliton pairs are photogenerated within ~250 fs with quantum efficiencies ($\phi_{ch}$) approaching unity. The excitation spectrum of $\phi_{ch}$ shows an onset at ~1.0 eV with a weak photon energy dependence up to 4.7 eV. The results are consistent with the ultrafast soliton formation predicted by Su and Schrieffer and with the Su-Schrieffer-Heeger threshold of $2E_g/\pi$ for soliton pair production. The recombination dynamics of charged solitons is very fast (initial decay $< 1$ ps) with a modest dependence on the pump photon energy.

## INTRODUCTION

The discovery of electrical conductivity in doped polyacetylene[1] initiated the field of semiconducting and metallic polymers. Motivated in part by their potential for use in applications, this novel class of materials, which combine the optical and electronic properties of semiconductors and metals with the mechanical properties and processability of polymers, continues to be the focus of an active field of research.[2]

Polyacetylene $(CH)_x$ is the simplest semiconducting (conjugated) polymer. The theoretical description of the degenerate ground state, the electronic structure and the soliton excitations of *trans*-$(CH)_x$ has been generalized to the broader class of semiconducting polymers in which the ground state degeneracy has been lifted. The successful model of Su, Schrieffer, and Heeger (SSH) (Ref. 3) treats the polymer chain as a tight-binding one-dimensional semiconductor in the one-electron approximation and explicitly includes the electron-phonon interaction, but neglects electron-electron (el-el) interactions, assuming they are relatively weak due to screening. The SSH model predicts that the lowest energy fundamental excitations in polyacetylene are solitons, self-localized by the electron-phonon interaction. The solitons in *trans*-$(CH)_x$ have a reversed spin-charge relationship; neutral solitons ($S^0$) have spin $\frac{1}{2}$, and charged solitons ($S^+,S^-$) have spin 0. The minimum energy required for creation of a soliton pair was calculated to be $2E_g/\pi$ within the SSH model, where $E_g$ is the $\pi$-$\pi^*$ energy gap. Solitons in polyacetylene have been studied experimentally by several techniques.[3]

Calculations by Su and Schrieffer[4] described the process of charged soliton pair formation subsequent to photoexcitation via the $\pi$-$\pi^*$ interband transition in *trans*-$(CH)_x$ with a photon energy ($h\nu$) equal to $E_g$. They showed that within ~100 fs, the lattice around a photoexcited electron-hole pair relaxes to form a well separated $S^+$-$S^-$ pair. Other calculations have shown that this picture remains correct when weak electron-electron interactions are included in the model.[5] The predicted ultrafast photogeneration of solitons

in *trans*-$(CH)_x$ has been confirmed with time-resolved spectroscopy.[6–9] These early ultrafast experiments used photoexcitation energies above the energy gap ($h\nu \gtrsim E_g$). However, direct photogeneration of soliton pairs can occur even for $2E_g/\pi < h\nu < E_g$, enabled by nonlinear zero-point motion of the lattice.[10] The absorption coefficient for direct soliton photoexcitation was predicted to be small near the threshold $2E_g/\pi$, and to increase exponentially as the photon energy approaches $E_g$.[11] If this is the dominant absorption process in the *trans*-$(CH)_x$ samples below the energy gap, one would expect that the quantum efficiency for charged soliton pair photogeneration ($\phi_{ch}$) to be unity for $2E_g/\pi < h\nu < E_g$ and, if the charged soliton pair is the lowest energy photoexcitation, well above $E_g$.

This issue has been addressed experimentally by measurements of steady-state photoinduced absorption (PIA) (Refs. 12 and 13) and photoconductivity,[14] yielding the excitation spectrum for charged soliton generation. The excitation spectrum drops exponentially from $E_g$ towards an onset at ~1.0 eV, and $\phi_{ch}$ was estimated to be only about 1% for energies above $E_g$. These results have been interpreted both in support of (since the onset is consistent with $2E_g/\pi$)[12] and against the SSH model (since $\phi_{ch} \sim 1\%$ at 2.0 eV and is reduced to 0.1% at 1.4 eV).[13] However, steady-state measurements do not probe the early time intrinsic photoexcitations, but only the long-lived solitons that are usually associated with traps due to defects and impurities.[5,9] Measurements with femtosecond time resolution are needed to obtain the excitation spectrum for intrinsic photogeneration of soliton pairs.

Here we use ultrafast photoinduced absorption by infrared-active vibrational (IRAV) modes,[15,16] an all-optical technique with subpicosecond time resolution carried out in zero applied electric field, to investigate soliton photogeneration and dynamics in oriented *trans*-polyacetylene. The IRAV absorption results from Raman-active vibrational modes that become infrared-active when the local symmetry is broken by self-localization of charges with associated changes in the bond lengths (e.g., soliton formation). The IRAV modes have a one-to-one correspondence with the

# Time-resolved measurements of photoinduced electron transfer from polyfluorene to $C_{60}$

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The excited state dynamics of polyfluorene and the dynamics of the photoinduced electron transfer from polyfluorene to a $C_{60}$ derivative have been studied with time-resolved pump-probe measurements at low excitation density. Using the stimulated emission and photoinduced absorption spectra, the decay of the neutral excited state and the growth of the ionic excited state have been time resolved; the photoinduced charge transfer reaction occurs with a characteristic time constant of approximately 3 ps.

## I. INTRODUCTION

Advances in ultrafast spectroscopic techniques[1,2] have enabled the study of photoinduced processes in semiconducting ($\pi$-conjugated) polymers in real time.[3] Ultrafast studies, using laser pulses with wavelengths in the spectral range from the ultraviolet-visible to the midinfrared, have contributed to the understanding of the underlying photophysics of this class of electronic polymers.[3–7]

Ultrafast photoinduced electron transfer from poly(phenylene vinylene) (PPV) and its soluble derivatives to $C_{60}$ and its derivatives has been reported.[8,9] The ultrafast charge transfer and the associated high quantum efficiency for charge separation provide a pathway for the development of high efficiency photodetectors and photovoltaic cells fabricated from $\pi$-conjugated polymers.[10] Moreover, since $C_{60}$ and its derivatives stabilize the charge separation by photoinduced electron transfer, the study of such polymer/$C_{60}$ mixtures creates an opportunity to probe the nature of the photoexcitations in semiconducting polymers.

In this work, the excited state dynamics of polyfluorene (PFO) and the dynamics of the photoinduced electron transfer from PFO to a $C_{60}$ derivative have been studied with time-resolved pump-probe experiments carried out under low excitation intensity. As high efficiency blue-emitting materials, the polyfluorenes are promising for use in full-color displays.[11] Moreover, copolymers of PFO are the only family of conjugated polymers that emit colors spanning the entire visible spectrum.[11]

We report here ultrafast measurements of the photoinduced transient absorption spectra of a blend of polyfluorene with a $C_{60}$ derivative. Both the decay of the neutral excited state and the growth of the ionic, charge-separated state have been time resolved. The photoinduced charge transfer reaction occurs with a time constant of approximately 3 ps.

## II. DETAILS OF THE EXPERIMENT

The ultrafast pump-probe experiments were performed using a Spectral-Physics amplified Ti:sapphire system to produce 150 fs (full-width at half-maximum) pulses with a center wavelength of 800 nm at a repetition rate of 1 kHz. The 800-nm beam was split into two parts. The stronger beam was frequency-doubled through a nonlinear (BBO) crystal to generate the 400-nm pump beam. The weaker beam was fo-

cused onto a 1-mm sapphire plate to generate the white light continuum which was also split, with one beam serving as the probe beam and the other serving as the reference beam. The probe was delayed with respect to the pump by a computer-controlled translation stage. The 400-nm pump was focused onto the sample with a beam size of ~500 $\mu$m. The probe beam was focused onto the same spot but with a smaller size to make certain that only the photoexcited region was probed. The signal was detected using a silicon photodiode and a lock-in amplifier after passing through an Oriel tunable bandpass filter (for 400–700 nm) or an interference filter (for 750 and 850 nm) to select the detection wavelength. Except for measurements of the pump fluence dependence, the pump beam was attenuated to ~10 $\mu$J/cm$^2$, well below the onset of bimolecular (fluence dependent) processes which are observed at fluence levels levels greater than 25 $\mu$J/cm$^2$. For all experiments, consecutive measurements at the same spot were carried out, and reproducible results were obtained; there was no observable optical damage during the measurements.

The poly(9,9-dioctylfluorene) (PFO) sample was purchased from American Dye Source, Inc. (ADS129BE). Several sources of PFO were examined. Care was taken to choose material with no indication of undesired green fluorenone emission between 2.2 and 2.4 eV.[12] The steady state spectra of the PFO films used in this study (cast from chloroform) are characteristic of the best available PFO.

The $C_{60}$ derivative, 1-(3-methoxycarbonyl)-propyl-1-phenyl[6,6]$C_{61}$ (PCBM) was obtained from Professor Fred Wudl (UCLA). All films (both pristine PFO and the PFO/$C_{60}$ blend) were prepared by spin-casting on quartz substrates from chloroform solution (10 mg/ml), with an optical density of ~1.2 at the absorption maximum. To prevent aggregation, the solution was heated to 65 °C for 10 min and then cooled to approximately room temperature before spin casting. The spin-cast films were subsequently baked for 1 h at 60 °C to remove any residual solvent. Using a dry/glove box filled with nitrogen, the sample was loaded into a vacuum chamber which was subsequently kept under a dynamic vacuum ($<10^{-5}$ mbar) during the experiment.

In these initial experiments, a PFO/C60 blend containing 17% weight/weight $C_{60}$ was chosen to study the electron transfer dynamics. At this concentration, the absorption at 400 nm is dominated by the PFO. Thus we can be confident that we are pumping into the $\pi$-$\pi^*$ transition of the PFO

# Direct observation of a time-delayed intermediate state generated via exciton-exciton annihilation in polyfluorene

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Excitation-density- and probe-wavelength-dependent pump-probe measurements are used to characterize the excited-state dynamics in pristine polyfluorene. At high excitation densities, a secondary excitation is created at times delayed from the initial formation of excitons. The spectrum of the intermediate state has been characterized by probe-wavelength-dependent measurements. We interpret the results in terms of the generation of charge-separated pairs via a two-step exciton-exciton annihilation process.

## I. INTRODUCTION

Semiconducting polymers have emerged as materials with interesting optical and electrical properties and promising applications, including light-emitting diodes, lasers, field-effect transistors, solar cells, etc.[1,2] Although extensive research has been carried out with the goal of understanding the photophysics of this class of materials, the nature of the elementary excitations in different semiconducting polymers remains controversial: neutral excitons or charge separated pairs? Debate has focused on the charge generation mechanism:[3] Are charges generated as primary excitations or via a secondary process involving exciton dissociation?

For polymers with PPV backbone structure, transient photoconductivity and ultrafast pump-probe measurements of the photoinduced infrared-active vibrational (IRAV) mode absorption[3-7] demonstrated that the exciton binding energy is less than 0.1 eV. Because of the small exciton binding energy, both neutral excitons and charge-separated pairs are within 100 fs following direct $\pi$-$\pi^*$ photoexcitation in the PPV's; e.g., the branching ratio for charge generation was determined to be ~10% in MEH-PPV.[5-7]

The soluble polyfluorene derivatives—for example, poly(9,9-dioctylfluorene) (PFO)—are high efficiency blue-emitting materials.[8] The polyfluorenes and related copolymers are the only known family of conjugated polymers that emit colors spanning the entire range of visible wavelengths. There is, however, limited information available on the photophysical properties of the polyfluorenes. In a previous publication,[9] we reported the results of a time-resolved study of the excited-state dynamics of pristine polyfluorene and the photoinduced electron transfer reaction from PFO to $C_{60}$. The results implied that at low excitation densities neutral excitons are the primary photogenerated species in PFO. We report here that at high excitation densities, the pump-probe signals show significantly different decay profiles and striking probe wavelength dependences. The generation of a secondary excitation (intermediate state) via exciton-exciton annihilation and its subsequent decay are directly observed. The spectrum of the intermediate state has been characterized by probe-wavelength-dependent measurements. We interpret the results in terms of the generation of charge-separated pairs via the following two-step exciton-exciton annihilation process:

$$E^* + E^* \rightarrow E^{**} \rightarrow (1-\eta)(E^* + Q) + \eta(p^- + p^+), \quad (1)$$

where $E^*$ represents an exciton, $E^{**}$ represents a higher-energy excited state, $Q$ is the heat generated during radiationless decay back to the single-exciton state, and $\eta$ is the fraction of the $E^* - E^*$ annihilation events that yield separated charged polaron pairs $(p^- + p^+)$.

## II. EXPERIMENTS

The ultrafast pump-probe instrumentation has been described in detail elsewhere.[9] Briefly, femtosecond pulses with a repetition rate of 1 kHz were derived from a Spectra-Physics amplified Ti:sapphire system. The 400-nm pump beam (generated by frequency doubling of the 800-nm output from the amplifier) was focused onto the sample with a beam size of ~500 $\mu$m. The probe beam, a white light continuum generated from self-phase modulation in a 1-mm sapphire plate, was focused onto the same spot, but with a smaller size (~100 $\mu$m) to make certain that only the photoexcited region was probed. The delay between the pump and probe pulses was varied by a computer-controlled translation stage. The signal was detected using a silicon photodiode and a lock-in amplifier after passing through an Oriel tunable bandpass filter (400–700 nm) or interference filters to select the detection wavelength.

The poly(9,9-dioctylfluorene) sample was purchased from American Dye Source, Inc. and carefully characterized for purity. The films were prepared by spin-casting onto quartz substrates from chloroform solution (10 mg/ml), with an optical density of ~1.2 at the absorption maximum (~384 nm). The PFO emission spectrum spans from 400 to 500 nm with peaks at ~418 and ~435 nm. Thus the emission was that of pure PFO with no sign of the energy-shifted peak often observed in the polyfluorenes.[10] The films were prepared and handled in a controlled atmosphere glove box filled with nitrogen and were loaded into a vacuum chamber which was kept under dynamic vacuum ($<10^{-5}$ mbar) during the experiment.

## III. RESULTS AND DISCUSSION

### A. Excitation density dependence at 480 nm probe wavelength

Excitation-density-dependent time-resolved experiments have been reported for a number of semiconducting

# Origin of efficient light emission from a phosphorescent polymer/organometallic guest-host system

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Time-resolved photoinduced absorption measurements were performed at 77 K and room temperature on thin films of tris[9,9-dihexyl-2-(phenyl-4'-(-pyridin-2"-yl)fluorene]iridium(III) [Ir(DPPF)$_3$] doped into a blend of poly($N$-vinylcarbazole) (PVK) with 2-(4-biphenylyl)-5-(4-tert-butylphenyl)-1,3,4-oxadiazole (PBD). We observe that in the PVK-PBD host blend, charge trapping (CT) plays an important role in the excited-state dynamics, in addition to exciplex formation and intensity-dependent decay of primary excitations. We develop a physical model which includes all interactions and which is in excellent agreement with the data. We find that 35% of the initial photoexcitation channels into CT states and that exciplexes are formed at a rate of 1/10 ps$^{-1}$. For the Ir(DPPF)$_3$ doped host composite, we write the rate equations for all population densities (which include the above excited-state species) and include energy-transfer rates from the host to the guest molecules. In both 0.2% and 2% Ir(DPPF)$_3$:(PVK-PBD) blends, Förster energy-transfer rates drop to half their low-temperature values at room temperature. We attribute this difference to a limited availability of guest molecules ready for energy transfer following charge trapping and insufficient spectral overlap due to shifts in the highest occupied and lowest unoccupied molecular orbital levels of the guest upon hole trapping. We conclude that the overall host-guest energy transfer is almost complete at room temperature in the 2% phosphorescent blend, with a large contribution (35%) from CT states which exhibit emission at all probe wavelengths.

## I. INTRODUCTION

Phosphorescent dopants have been successfully used in organic light-emitting diodes (OLED's) to improve the device performance by breaking the spin conservation rule. The resulting harvesting of both singlet and triplet excitons has led to very high-efficiency OLED's.[1-13] One of the most promising guest-host systems uses the phosphorescent-guest tris[9,9-dihexyl-2-(phenyl-4'-(-pyridin-2"-yl)fluorene]iridium(III) [Ir(DPPF)$_3$, Fig. 1(a)] into a host blend comprising poly($N$-vinylcarbazole) [PVK, Fig. 1(b)] with 2-(4-biphenylyl)-5-(4-tert-butylphenyl)-1,3,4-oxadiazole [PBD, Fig. 1(c)]. Because of the strong spin-orbit coupling of the heavy metal center, Ir complexes have efficient phosphorescence and short lifetimes, which typically range from 1 to 14 $\mu$s. In this study, we investigate in detail the physical processes involved in the high performance of Ir(DPPF)$_3$-doped OLED's. On a sub-nanosecond time scale, ultrafast pump-probe spectroscopy offers key information on how the photoexcitation is transferred from the polymer host to the organometallic phosphor guest.

When designing a host-guest system, one has to carefully analyze its ability to transfer the initial excitation (optical or electrical pumping) from the host material ("blue emitter") to the dilute guest species which emit at longer wavelengths. The emission of the blend will be redshifted, with a twofold benefit: minimum reabsorption losses and tunable emission color with the use of various dopant chromophores. Often, the mechanism behind the observed photoluminescence (PL) spectra of polymer blends is the transfer of energy from host to guest via the long-range dipole-dipole interaction, known as Förster energy transfer.[14-16] As a result, complete, rapid energy transfer can occur even at dilute concentrations of the

guest.[17,18] In electroluminescence (EL), following injection of the carriers, direct electron and hole trapping plays a role, and an excited dopant molecule is formed by the sequential trapping of a hole and then an electron onto the guest organometallic complex.
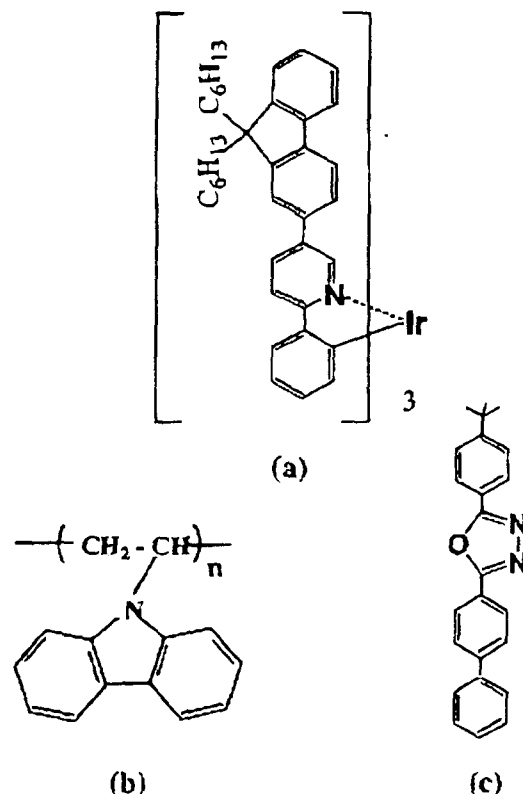


FIG. 1. Chemical structures of (a) Ir(DPPF)$_3$, (b) PVK, and (c) PBD.

# Ultrafast studies of the photophysics of semiconducting polymers

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## 1. – Photoinduced IRAV: ultrafast photogeneration of charged polarons

Semiconducting (conjugated) polymers have been known for over twenty years. Research on these materials has intensified in the last decade as a result of the increasing number of applications, including light-emitting diodes, lasers and solar cells [1]. Despite many advances, the nature of the elementary excitations in semiconducting polymers remains controversial [2]. Issues of great importance to the understanding and improvement of polymer devices, such as the exciton binding energy and charge carrier generation mechanism, remain unresolved. Here we use a unique all-optical technique [3,4] based on photoinduced infrared-active vibrational (IRAV) modes to study the photogeneration and recombination dynamics of charged polarons in poly(paraphenylene-vinylene), PPV, and its derivatives.

There are two dominant theoretical views of the charge generation mechanism in conjugated polymers [2,5]. The first is based on the model of Su, Schrieffer and Heeger (SSH) [6], which treats the polymer chain as a tight-binding one-dimensional semiconductor in the one-electron approximation and explicitly includes the electron-phonon interaction. The SSH approach assumes that the electron-electron (el-el) interactions are relatively weak because of screening, leading to small exciton binding energies ($\approx 0.1$ eV) [7].